

Microscopic origin of the jump diffusion model

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Abstract

The present paper is aimed at studying the microscopic origin of the jump diffusion. Starting from the N -body Liouville equation and making only the assumption that molecular reorientation is overdamped, we derive and solve the new (hereafter generalized diffusion) equation. This is the most general equation which governs orientational relaxation of an equilibrium molecular ensemble in the hindered rotation limit and in the long time limit. The generalized diffusion equation is an extension of the small-angle diffusion equation beyond the impact approximation. We establish the conditions under which the generalized diffusion equation can be identified with the jump diffusion equation, and also discuss the similarities and differences between the two approaches.

I. INTRODUCTION

How do the molecules reorient in water? Certainly, their rotation is significantly hindered and the orientational correlation functions (OCFs) exhibit the long time exponential decay. It would not be thus unreasonable to expect that the small-angle rotational diffusion would accurately describe reorientation of water molecules. On the contrary, the very first molecular dynamics simulations have revealed that water reorientation hardly obeys the small-angle diffusion.^{1,2} In fact, virtually all the simulations performed so far on liquid water support the jump-diffusion mechanism of reorientation of water molecules.^{3,4,5,6} Very recently, a new approach has been developed, which views rotation of water molecules in terms of breaking and making of hydrogen bonds, and the extended jump-diffusion model has been put forward.^{7,8,9,10}

Two fundamental questions arise then: What is wrong with the small-angle diffusion? And why is the jump diffusion applicable to water reorientation? Indeed, the small-angle diffusion^{11,12,13,14,15,16,17} is well known to be a legitimate description of molecular reorientation in the overdamped limit, i.e. when the angular momentum is a fast variable on the timescale of reorientation. Then the integral relaxation time of the angular momentum correlation function yields, through the Green-Kubo relation, the small angle rotational diffusion coefficient.^{11,12,13,14,15,16,17} For liquid water, the integral angular momentum relaxation time (\sim a few femtoseconds) is much shorter than the orientational relaxation time (\sim several picoseconds), so that the small-angle diffusion should perform excellently. It does not, however.

The jump diffusion^{18,19,20,21,22} is formulated through the master equation in the space of orientations. The ensuing OCFs are specified by the two phenomenological parameters, the averaged jump angle and the jump rate. The parameters do not have any molecular origin or specificity. They can hardly be traced back or even related to moments of inertia or rotational friction. The very notions of angular momentum and rotational relaxation are alien to the jump diffusion. It is thus surprising that such a model, which is normally used for a phenomenological description of molecular reorientations in solids and glasses, is applicable to liquid water.

The present paper is aimed at studying the microscopic origin of the jump diffusion and explaining the failure of the small-angle diffusion. Starting from the N -body Liouville

equation and making only the assumption that molecular reorientation is overdamped (a precise meaning of this requirement is concretized in Sec. 4), we derive and solve the new (hereafter generalized diffusion) equation. This is the most general equation which governs orientational relaxation of an equilibrium molecular ensemble in the hindered rotation limit and in the long time limit. Similarly to the small-angle and jump diffusion, the generalized diffusion equation predicts exponentially decaying OCFs. The generalized diffusion equation is an extension of the small-angle diffusion equation beyond the impact approximation. It can be rewritten as the small-angle diffusion equation, in which the diffusion coefficients depend explicitly on the rank j of the OCF. We establish the conditions under which the generalized diffusion equation can be identified with the jump diffusion equation, and also discuss the similarities and differences between the two approaches.

II. GENERALIZED MASTER EQUATION

We start with a formally exact Zwanzig-type master equation, which can be derived from the N -particle rotation-translational Liouville equation by applying the projection operator technique^{23,24,25}

$$\partial_t \rho(\mathbf{J}, \mathbf{\Omega}, t) = -i\Lambda(\mathbf{J}, \mathbf{\Omega})\rho(\mathbf{J}, \mathbf{\Omega}, t) - \int_0^t dt' \mathcal{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\mathbf{\Omega}), t - t')\rho(\mathbf{J}, \mathbf{\Omega}, t'). \quad (1)$$

Here $\rho(\mathbf{J}, \mathbf{\Omega}, t)$ is the single particle probability distribution, \mathbf{J} is the angular momentum in the molecular frame, $\hat{\mathbf{L}}(\mathbf{\Omega})$ is the angular momentum operator in the molecular frame, $\mathbf{\Omega}$ denotes collectively the set of three Euler angles α, β, γ that specify orientation of the molecular frame with respect to the laboratory one. The free-rotor Liouville operator consists of the two contributions,

$$\Lambda(\mathbf{J}, \mathbf{\Omega}) = \Lambda_{\mathbf{\Omega}} + \Lambda_{\mathbf{J}}, \quad (2)$$

which describe, respectively, the angular momentum driven reorientation and the angular momentum change during free rotation:

$$\Lambda_{\mathbf{\Omega}} = \sum_{a=x,y,z} I_a^{-1} J_a \hat{L}_a(\mathbf{\Omega}), \quad \Lambda_{\mathbf{J}} = -i \sum_{a,b,c=x,y,z} \varepsilon_{abc} I_b^{-1} J_a J_b \partial_{J_c}, \quad (3)$$

I_α are the main moments of inertia, ε_{abc} is the Levi-Civita symbol. $\Lambda_{\mathbf{J}} \equiv 0$ for linear and spherical rotors.

The relaxation operator \mathfrak{R} can explicitly be written as the generalized Fokker-Planck operator^{23,24,25}

$$\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) = \sum_{a=x,y,z} \partial_{J_a} \Xi_a(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) (\partial_{J_a} + J_a I_a^{-1}), \quad (4)$$

$\Xi_a(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t)$ being a friction operator (for a standard rotational Fokker-Planck equation, $\Xi_a(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) = \delta(t) \xi_a$, where ξ_a is the constant friction). As is clear from Eq. (4), the relaxation operator obeys the normalization

$$\int d\mathbf{J} \mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) = 0 \quad (5)$$

(note that integration over $\boldsymbol{\Omega}$ is not necessary) and the detailed balance

$$\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) \rho_{eq}(\mathbf{J}) = 0. \quad (6)$$

$\rho_{eq}(\mathbf{J})$ is the equilibrium Boltzmann distribution

$$\rho_{eq}(\mathbf{J}) = (2\pi k_B T)^{-3/2} (I_x I_y I_z)^{-1/2} \exp\left\{-\sum_{a=x,y,z} J_a^2 / (2k_B T I_a)\right\}. \quad (7)$$

k_B is the Boltzmann constant, T is the temperature.

Due to the isotropy of space, the relaxation operator $\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t)$ cannot depend on the Euler angles $\boldsymbol{\Omega}$ explicitly.²⁶ However, it can explicitly contain the angular momentum operators.^{23,24,25,27} The bulk majority of the theories of molecular rotation (except the jump-diffusion models^{18,19,20,21,22} and some more general approaches^{23,24,25,27}), adopt the impact approximation, which assumes that \mathfrak{R} is independent of $\hat{\mathbf{L}}(\boldsymbol{\Omega})$.^{28,29} As will be clear from the following discussion, retaining the $\hat{\mathbf{L}}(\boldsymbol{\Omega})$ -dependence in the relaxation operator is essential for getting beyond the small-angle diffusion.

III. ORIENTATIONAL CORRELATION FUNCTIONS

If we expand the probability density on the Wigner D-matrices of the rank j ,³⁰

$$\rho(\mathbf{J}, \boldsymbol{\Omega}, t) = \sum_{j=0}^{\infty} \frac{2j+1}{8\pi^2} \sum_{k,l=-j}^j \rho_{kl}^j(\mathbf{J}, t) D_{kl}^{*j}(\boldsymbol{\Omega}), \quad (8)$$

we arrive at the equation

$$\partial_t \rho^j(\mathbf{J}, t) = -i(\Lambda_{\boldsymbol{\Omega}}^j + \Lambda_{\mathbf{J}}) \rho^j(\mathbf{J}, t) - \int_0^t dt' \mathfrak{R}^j(\mathbf{J}, \partial_{\mathbf{J}}, \mathbf{L}^j, t-t') \rho^j(\mathbf{J}, t'). \quad (9)$$

Here Λ_{Ω}^j and \mathfrak{R}^j are determined by Eqs. (2) and (3), in which the angular momentum operators \hat{L}_a are replaced by their matrix elements L_a^j over the D-matrices:

$$(L_x^j)_{kl} \pm i(L_y^j)_{kl} = \delta_{k,l \mp 1} \{(j \pm l)(j \mp l + 1)\}^{1/2}, \quad (L_z^j)_{kl} = l\delta_{kl}; \quad -j \leq k, l \leq j. \quad (10)$$

In Eq. (9) and below, we use the compact notation, regarding operators Λ_{Ω}^j , \mathfrak{R}^j and the probability density $\rho^j(t)$ as $(2j+1) \times (2j+1)$ matrices, so that the product $\Lambda_{\Omega}^j \rho^j$ and similar quantities are to be understood as the matrix products.

If the impact approximation is used, then the relaxation operator is j -independent,

$$\mathfrak{R}^j = \mathfrak{R}^0. \quad (11)$$

Since the relaxation operator \mathfrak{R} is, in general, $\hat{\mathbf{L}}(\Omega)$ -dependent, rotational and orientational relaxation is described by a collection of rank-dependent operators \mathfrak{R}^j . Despite the j -dependence of \mathfrak{R}^j is normally ignored, its very presence is not entirely unexpected, since OCFs of different ranks are affected by the effective j -dependent cage potentials.^{31,32} Thus a popular librational oscillator model of Lynden-Bell and Steele requires j -dependent values of the librational frequencies and mean torques for reproducing simulated OCFs even for simple liquids.³³ Dielectric friction, which governs orientational relaxation in polar systems, is also known to be rank-dependent.³⁴ Furthermore, the quantum master equations are subdivided into j -dependent sub-operators even within the impact approximation.²⁸

OCF of the rank j can be calculated through $\rho^j(t)$ as follows:

$$\langle P_j(\mathbf{u}_1(0)\mathbf{u}_2(t)) \rangle \equiv \sum_{k,l=-j}^j D_{0k}^j(0, -\alpha_2, -\beta_2) \rho_{kl}^j(t) D_{l0}^j(\alpha_1, \beta_1, 0). \quad (12)$$

Here P_j is the Legendre polynomial, α_i, β_i are the spherical angles of the unit vectors \mathbf{u}_i ($i = 1, 2$) in the molecular frame,

$$\rho_{kl}^j(t) \equiv \int d\mathbf{J} \rho_{kl}^j(\mathbf{J}, t), \quad \rho^j(\mathbf{J}, t=0) = \rho_{eq}(\mathbf{J}). \quad (13)$$

If we wish to follow reorientation of the unit vector pointing along the molecular z -axis, then $\alpha_i = \beta_i = 0$ and

$$\langle P_j(\mathbf{u}_z(0)\mathbf{u}_z(t)) \rangle = \rho_{00}^j(t). \quad (14)$$

IV. OVERDAMPED LIMIT AND GENERALIZED DIFFUSION

Taking the Laplace transform of Eq. (9), we get the equivalent equation

$$-\rho_{eq}(\mathbf{J}) + s\tilde{\rho}^j(\mathbf{J}, s) = -i(\Lambda_{\Omega}^j + \Lambda_{\mathbf{J}})\tilde{\rho}^j(\mathbf{J}, s) - \tilde{\mathfrak{R}}^j\tilde{\rho}^j(\mathbf{J}, s) \quad (15)$$

(hereafter, all the Laplace-transformed operators are denoted by tilde, viz. $\tilde{f}(s) = \int_0^\infty dt \exp\{-st\}f(t)$ for $\forall f(t)$). Now we are in a position to introduce the projection operators

$$P = \rho_{eq}(\mathbf{J}) \int d\mathbf{J} \dots, \quad Q = 1 - P. \quad (16)$$

Evidently, $P\tilde{\mathfrak{R}}^j = \tilde{\mathfrak{R}}^jP = 0$ due to the normalization (5) and detailed balance (6), respectively. Applying P and Q to Eq. (15) and making use of the identities $P\Lambda_{\mathbf{J}} = \Lambda_{\mathbf{J}}P = 0$, we obtain the following exact equation for $\tilde{\rho}^j(s) = \rho_{eq}^{-1}(\mathbf{J})P\tilde{\rho}^j(\mathbf{J}, s)$:

$$\tilde{\rho}^j(s) = \{s + \tilde{M}^j(s)\}^{-1} \quad (17)$$

with

$$\tilde{M}^j(s) = \int d\mathbf{J} \Lambda_{\Omega}^j \{s + iQ\Lambda_{\Omega}^j + i\Lambda_{\mathbf{J}} + \tilde{\mathfrak{R}}^j(s)\}^{-1} \Lambda_{\Omega}^j \rho_{eq}(\mathbf{J}). \quad (18)$$

Since rotation is hindered, it is natural to assume that the streaming operators can be neglected as compared to the relaxation operator, $\tilde{\mathfrak{R}}^j(s)$:

$$\|Q\Lambda_{\Omega}^j\|, \|\Lambda_{\mathbf{J}}\| \ll \|\tilde{\mathfrak{R}}^j(s)\| \quad (19)$$

(here $\|...\|$ is a suitably defined operator norm). Then, making use of the explicit form of the streaming operator Λ_{Ω}^j (2), we can write

$$\tilde{M}^j(s) = k_B T \sum_{a=x,y,z} \frac{(L_a^j)^2}{I_a} \tilde{C}_{J,a}^j(s), \quad (20)$$

$$\tilde{C}_{J,a}^j(s) = \frac{\langle J_a \{s + \tilde{\mathfrak{R}}^j(s)\}^{-1} J_a \rangle}{\langle J_a^2 \rangle}. \quad (21)$$

The quantity $C_{J,a}^{(j)}(t)$ can be termed as the generalized angular momentum correlation function. It yields the standard angular momentum correlation function for $j = 0$. Within the impact approximation (11), $\tilde{\mathfrak{R}}^j$ is j -independent, so that $C_{J,a}^{(j)}(t)$ for different j are all the same and coincide with $C_{J,a}^{(0)}(t)$. In such a case, Eq. (17) describes the diffusion equation with memory.^{13,28,35,36}

If we are interested in the long-time behavior of OCFs, we can neglect the non-Markovian effects, substitute $\tilde{\mathfrak{R}}^j(s)$ by $\tilde{\mathfrak{R}}^j(0)$, and invert Eq. (17) into the time domain. If the memory operator is defined via Eqs. (20) and (21), we then arrive at the generalized diffusion formula

$$\rho^j(t) = \exp\{-\tilde{M}^j(0)t\} \equiv \exp\left\{-\sum_{a=1}^3 (L_a^j)^2 \mathcal{D}_a^j t\right\}. \quad (22)$$

Here \mathcal{D}_a^j are the j -dependent generalized diffusion constants, which are uniquely determined by the generalized angular momentum integral relaxation times $\tau_{J,a}^j$:

$$\mathcal{D}_a^j \equiv \tau_{J,a}^j \frac{k_B T}{I_a}, \quad \tau_{J,a}^j \equiv \tilde{C}_{J,a}^j(0) \equiv \frac{\langle J_a \{ \tilde{\mathfrak{R}}^j(0) \}^{-1} J_a \rangle}{\langle J_a^2 \rangle} \equiv \int_0^\infty dt C_{J,a}^{(j)}(t). \quad (23)$$

Eq. (23) can be coined as the generalized Green-Kubo relation.

If $\tilde{\mathfrak{R}}^j(0)$ is j -independent (that is, the impact approximation (11) holds), then the small-angle diffusion is recovered from Eq. (22):

$$\rho^j(t) = \exp\left\{-\sum_{a=1}^3 (L_a^j)^2 \mathcal{D}_a t\right\}, \quad (24)$$

$$\mathcal{D}_a \equiv \tau_{J,a}^{(0)} \frac{k_B T}{I_a}. \quad (25)$$

A close similarity between Eqs. (22) and (24) is evident. A major difference is the following: the generalized angular momentum relaxation times $\tau_{J,a}^j$ are not necessarily equaled to the angular momentum relaxation times $\tau_{J,a}^{(0)}$ any longer. Same is true about the diffusion coefficients \mathcal{D}_a^j and \mathcal{D}_a . Thus, the small-angle rotational diffusion is not applicable in the overdamped limit if the $\hat{\mathbf{L}}(\boldsymbol{\Omega})$ -dependence of the relaxation operator $\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t)$ cannot be ignored.

The generalized (22) and small-angle (24) diffusion equations allow us to analytically calculate OCFs (14) of the first ($j = 1$) and second ($j = 2$) rank for general asymmetric top molecules (see Appendix A).

V. JUMP DIFFUSION MODEL

The jump diffusion model^{18,19,20,21,22} can be retrieved from the general master equation (1), provided we chose the angular momentum independent relaxation operator

$$\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t) = \delta(t) \nu \mathfrak{R}_{\Omega}(\hat{\mathbf{L}}(\boldsymbol{\Omega})) \quad (26)$$

(ν being the jump rate) or if we consider any operator $\mathfrak{R}_\Omega(\hat{\mathbf{L}}(\Omega), t)$ with a finite memory in the long time limit. The jump diffusion operator (26) obeys the detailed balance

$$\mathfrak{R}_\Omega(\hat{\mathbf{L}}(\Omega))1 = 0 \quad (27)$$

(an isotropic distribution must be an eigenvector of \mathfrak{R}_Ω) and normalisation

$$\int d\Omega \mathfrak{R}_\Omega(\hat{\mathbf{L}}(\Omega)) = 0. \quad (28)$$

Note that the detailed balance (27) and normalization (28) conditions for operator \mathfrak{R}_Ω differ from their counterparts (5) and (6) for the true relaxation operator $\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\Omega), t)$. Therefore, the ensuing behaviours of the OCFs are different, too. Indeed, if we apply the hindered rotation limit (19) to Eq. (1) with the relaxation operator (26), we can simply neglect the streaming operator (2) as compared to the relaxation operator. Then, if we expand Eq. (8) over the Wigner matrices, we get the jump diffusion OCF

$$\rho^j(t) = \exp\{-\nu \mathfrak{R}_\Omega^j t\}. \quad (29)$$

Here \mathfrak{R}_Ω^j is the matrix element of the operator \mathfrak{R}_Ω over the Wigner matrices. It is frequently assumed that \mathfrak{R}_Ω^j can be parametrized through the averaged rotational matrix,

$$\mathfrak{R}_\Omega^j = 1 - \int d\mathbf{g} \rho(\mathbf{g}) \exp\{-i \sum_{a=x,y,z} g_a L_a^j\}. \quad (30)$$

The modulus and direction of \mathbf{g} determine the angle and axis of rotation, $\rho(\mathbf{g})$ is the corresponding probability density, and L_a^j are given by Eq. (10). The jump diffusion model reduces to the small-angle diffusion in the limit of small angular jumps ($\rho(\mathbf{g})$ is nonzero for $|g| \ll 1$). In case of isotropic jumps ($\rho(\mathbf{g}) = \rho(|\mathbf{g}|)$) we get, approximately,^{7,18,19,20,21,22}

$$\mathfrak{R}_\Omega^j = 1 - \frac{1}{2j+1} \frac{\sin((j+1/2)g)}{\sin(g/2)}, \quad (31)$$

g being an averaged jump angle.

VI. GENERALIZED DIFFUSION VS. JUMP DIFFUSION

We now establish the similarities and differences between the generalized diffusion and the jump diffusion. Both of the models predict exponentially decaying OCFs. The decay

rates are governed by the relaxation matrices $\widetilde{M}^j(0)$ (23) and $\nu\mathfrak{R}_\Omega^j$ (30) which, in general, differ from the small-angle diffusion tensor (25). One might thus prematurely conclude that both the generalized and the jump diffusion models result in the same predictions, and the use of any of the two is just a matter of taste. That is not the case, however. There are several important differences between the two approaches.

(i). The generalized diffusion tensor $\widetilde{M}^j(0)$ is inversely proportional to the dissipation strength. It is given, in fact, by the inverse of the relaxation operator $\widetilde{\mathfrak{R}}^j(0)$ (23). The jump diffusion tensor $\nu\mathfrak{R}_\Omega^j$ is proportional to the jump rate ν . This means that increase of dissipation (e.g., increase of molecular density) slows down the OCF decay in the generalized diffusion model but speeds up the OCF decay in the jump diffusion model.

(ii). The rank-dependence of $\widetilde{M}^j(0)$ is determined by the relaxation operator $\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t)$. It can be rather complicated, and it is not guaranteed that the functional form of $\widetilde{M}^j(0)$ can successfully be approximated by the jump-diffusion matrix \mathfrak{R}_Ω^j (30) or (31).

(iii). $\widetilde{M}^j(0)$ is explicitly determined by the angular momentum relaxation through the j -dependent generalized angular momentum relaxation times $\tau_{J,a}^j$ (23). Furthermore, $\widetilde{M}^j(0)$ depends explicitly on the molecular moments of inertia and on temperature. No such information is contained in the jump relaxation matrix \mathfrak{R}_Ω^j without additional ad hoc assumptions.

To better illustrate the similarities and differences between the generalized diffusion and the jump diffusion, we consider below two representative examples.

A. Liquid of spherical molecules

Starting from the N -(spherical) particle Liouville equation, Evans has obtained the $\hat{\mathbf{L}}(\boldsymbol{\Omega})$ -dependent corrections to the relaxation operator by expanding $\mathfrak{R}(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\boldsymbol{\Omega}), t)$ in powers of the (projected) streaming operator Λ_Ω (2) up to the second order.²⁴ Having utilized several other approximations, he has derived the explicit expression for the relaxation operator, which in our notation reads

$$\widetilde{M}^j(0) = \frac{j(j+1)\tau_J}{I/(k_B T) + (j(j+1) - 1/2)\tau_J^2 + j(j+1)\tau_T^2}, \quad (32)$$

τ_T being the torque relaxation time. This expression can equivalently be rewritten as $\widetilde{M}^j(0) = j(j+1)D^j$, where $D^j = \tau_J^{(j)}k_BT/I$ is the j -dependent diffusion coefficient and the generalized angular momentum relaxation time is defined as

$$\tau_J^{(j)} = \frac{\tau_J}{1 + (k_BT/I)[(j(j+1) - 1/2)\tau_J^2 + j(j+1)\tau_T^2]}. \quad (33)$$

If $\sqrt{I/(k_BT)} \gg \tau_J, \tau_T$, then we recover the small-angle diffusion (24) with the rank-independent diffusion coefficient (25). Now we can try to recast Eq. (32) in terms of the jump diffusion model relaxation operator $\nu \mathfrak{R}_\Omega^j$. The result is quite obvious in the opposite limit of $\sqrt{I/(k_BT)} \ll \tau_J$ or τ_T .³⁷ In such a case, the generalized diffusion relaxation operator becomes, approximately, j and temperature independent, and we recover the so-called large-angle jump limit of Eqs. (29)-(31):

$$\nu \approx \frac{\tau_J}{\tau_J^2 + \tau_T^2}, \quad g_j \approx \frac{2\pi}{2j+1}, \quad \mathfrak{R}_\Omega^j \approx 1, \quad (34)$$

so that the effective mechanism of molecular reorientation is via large-amplitude jumps. However, to make a connection with the jump diffusion model, we have to introduce a j -dependent averaged angle g_j (34). In all the intermediate situations ($\sqrt{I/(k_BT)} \sim \tau_J \sim \tau_T$) it is quite problematic to recast Eq. (32) into the jump diffusion relaxation operator form (29) and to make a clear partitioning between the jump rate ν and the jump matrix \mathfrak{R}_Ω^j . Anyway, even if we do so, then ν and \mathfrak{R}_Ω^j become temperature, τ_J , and τ_T -dependent. In a sense, such a dynamic information is alien to the jump diffusion model and must be incorporated into it ad hoc. Summarizing, the differences in predictions of the generalized diffusion model and the jump diffusion model are expected to be pronounced for liquids, in which the angular momentum relaxation time is comparable with the corresponding torque relaxation time.

B. Liquid water

Smishchev and Kusalik³⁸ have performed room-temperature molecular dynamics simulations of SPC/E liquid water and calculated the small-angle diffusion coefficients \mathcal{D}_a and orientational relaxation times τ_a^j of the first and second rank. For convenience, their data are collected in Table I.

If we wish to interpret the data in terms of the generalized diffusion model, we can recalculate \mathcal{D}_a into the angular momentum relaxation times $\tau_{J,a}^0$ via Eq. (25), as well as to

recalculate τ_a^j into the generalized angular momentum relaxation times $\tau_{J,a}^j$ via Eqs. (A8) and (23). The results are presented in Table II. Clearly, the water reorientation does not obey the small-angle diffusion: If this were the case, all $\tau_{J,a}^j$ ($j = 0, 1, 2$) would be the same. In reality, the generalized angular momentum relaxation times $\tau_{J,a}^1$ and $\tau_{J,a}^2$ are three-four times smaller than the corresponding angular momentum relaxation times $\tau_{J,a}^0$. Thus, the small-angle diffusion predicts that water molecules reorient much faster than they do in reality. Interestingly, $\tau_{J,a}^1 \approx \tau_{J,a}^2$ for $a = x, z$.

According to the data of Table I, $\tau_y^1/\tau_y^2 = 2.9$. Given this result alone, one could prematurely assume that reorientation of water molecules around their axes of the intermediate moment of inertia obeys the small angle diffusion. In reality, such a reorientation process has nothing to do with the small angle diffusion, since the angular momentum relaxation time $\tau_{J,y}^0$ exceeds the generalized angular momenta relaxation times $\tau_{J,y}^1$ and $\tau_{J,y}^2$ by the factor of 2.6 and 3.8, correspondingly (see Table II). This is a nice illustration of how misleading can be uncritical application of the small-angle diffusion beyond its domain of validity.

We can also try to interpret the results of Svishchev and Kusalik³⁸ in terms of the jump diffusion model. As is clear from Table I and as is confirmed by other computer simulations^{4,6,39} and NMR experiments,³⁹ reorientation of water molecules is significantly anisotropic. Therefore, it is impossible to describe all six orientational relaxation times τ_a^j ($a = x, y, z$; $j = 1, 2$) by a single set of the jump angle g (Eq. (31)) and rate ν . The extensions of the jump-diffusion model developed in Refs.^{21,22} make it possible to describe anisotropic jumps. For our purposes, it is more convenient to introduce the axis-dependent jump angles g_a , $a = x, y, z$.⁶ Given essential nonsphericity of water molecules and anisotropy of their hydrogen bonding network, this assumption is not unrealistic. For each $a = x, y, z$, we should find g_a and ν which, according to Eqs. (29) and (A6), fit τ_a^j from Table I via the expression $\tau_a^j = \{\nu \mathcal{R}_\Omega^j\}^{-1}$. The results of this procedure are presented in Table III. The jump rate ν , by its definition, should be the same for all τ_a^j . As is seen from Table III, it is impossible to meet this requirement because we get the axis-dependent rates ν_a . According to the generalized jump-diffusion model, we should additionally take into account the slow reorientation of the O...O vector of the pair of H-bonded water molecules.^{7,8,9} This appears to make the differences in ν_a smaller, but the problem remains.⁶ Therefore, interpretation and explanation of the anisotropy of water reorientation in terms of the jump diffusion encounters significant difficulties.

The above results do not allow us to ascertain that the generalized diffusion model is superior over the jump diffusion model in the interpretation of reorientation of water molecules. Indeed, the generalized diffusion model does not allow us, within itself, to calculate the generalized angular momentum relaxation times $\tau_{J,a}^j$. On the other hand, the use of the (generalized) jump diffusion model for the explanation of rotational dynamics of water molecules has a microscopic justification since both ν and \Re_{Ω}^j can *independently* be extracted from molecular dynamics simulations, at least for the OH bond reorientation.^{7,8} Furthermore, numerical values of the rotational diffusion coefficients and orientational relaxation times presented in Table I should not be taken as ultimate benchmark data, since different water force fields predict different values of the quantities.⁴ However, the results of the present section show clearly that the generalized diffusion model allows us to get some insight into the process of reorientation of water molecules.

VII. CONCLUSION

We have derived the generalized diffusion equation (22), which is uniquely obtained from the many-particle Liouville equation in the overdamped rotation limit and in the long time limit. A precise meaning of the “overdamped limit” is given by inequalities (19). Eq. (22) predicts the exponentially decaying OCFs and reduces to the small-angle diffusion equation (24) provided that the relaxation operator $\Re(\mathbf{J}, \partial_{\mathbf{J}}, \hat{\mathbf{L}}(\Omega), t)$ is independent of the angular momentum operators $\hat{\mathbf{L}}(\Omega)$. In general, \Re is $\hat{\mathbf{L}}(\Omega)$ -dependent, and the small-angle diffusion does not hold. Eq. (22) is the most general equation which governs orientational relaxation of an equilibrium molecular ensemble in the hindered rotation limit and in the long time limit.

Any deviation from the small-angle diffusion behavior indicates the breakdown of the impact approximation (11). In such a case, the j -dependence of $\widetilde{M}^j(0)$ is determined by the interparticle interaction potential and is not established by the present analysis. However, we can get specific predictions if we assume that the deviation from the impact approximation is small. For the conceptual clarity, let us consider spherical molecules. Then we can expand the generalized angular momentum relaxation times τ_J^j around $j = 0$ and write

$$\widetilde{M}^j(0) = j(j+1) \frac{k_B T}{I} \tau_J^0 [1 + \lambda j(j+1)] + O(\lambda^2), \quad (35)$$

λ being a certain dimensionless, small, and j -independent parameter. The insertion of Eq. (35) into (22) gives us the generalized diffusion formula, and the ratio of the first- and second-rank orientational relaxation times is predicted to be $3 + 12\lambda + O(\lambda^2)$.

The generalized diffusion equation (22) can be mapped into the jump diffusion equation (29) if we identify $\widetilde{M}^j(0)$ (Eq. (20)) with the jump diffusion matrix $\nu \mathcal{R}_\Omega^j$ (Eqs. (30) and (31)). That can unequivocally be done in particular cases of small jumps and large-amplitude jumps. For example, Eq. (35) can be reproduced within the jump diffusion model if we put $\tau_j^0 k_B T / I = \nu(g^2/6)(1 + g^2/60)$ and $\lambda = -g^2/20$. In all intermediate situations, the use of the jump diffusion model requires additional justification, as is discussed in detail Sec. VI. Pragmatically speaking, if the actual OCFs of different ranks are well reproduced via Eqs. (29)-(31) with j -independent jump rates ν and angles g (as seems to be roughly the case for the reorientation of OH bond of a water molecule^{7,8}) then the jump diffusion model is a legitimate description for the long time exponential decays of OCFs. If the fitted g and (notably) ν have pronounced j -dependences, the use of the jump diffusion is dubious.

APPENDIX A: OCFS OF ASYMMETRIC TOP MOLECULES WITHIN SMALL-ANGLE AND GENERALIZED DIFFUSION MODELS

Within the small-angle diffusion model (24), OCFs (14) of the first ($j = 1$) and second ($j = 2$) rank are evaluated analytically for asymmetric top molecules^{11,14}

$$\langle P_1(\mathbf{u}_z(0)\mathbf{u}_z(t)) \rangle = \rho_{00}^1(t) = \exp\{-(\mathcal{D}_x + \mathcal{D}_y)t\}. \quad (\text{A1})$$

$$\langle P_2(\mathbf{u}_z(0)\mathbf{u}_z(t)) \rangle = \rho_{00}^2(t) = g_+ \exp\{-(6\mathcal{D} + 2\Delta)t\} + g_- \exp\{-(6\mathcal{D} - 2\Delta)t\}. \quad (\text{A2})$$

Here the following parameters are introduced:

$$\Delta = \sqrt{\mathcal{D}_x^2 + \mathcal{D}_y^2 + \mathcal{D}_z^2 - \mathcal{D}_x\mathcal{D}_y - \mathcal{D}_y\mathcal{D}_z - \mathcal{D}_z\mathcal{D}_x}, \quad (\text{A3})$$

$$\mathcal{D} = (\mathcal{D}_x + \mathcal{D}_y + \mathcal{D}_z)/3, \quad g_\pm = \frac{2\Delta \pm 3(\mathcal{D} - \mathcal{D}_z)}{4\Delta}. \quad (\text{A4})$$

Eqs. (A1) and (A2) can (approximately) be recast into the spherically-symmetric form

$$\langle P_j(\mathbf{u}_z(0)\mathbf{u}_z(t)) \rangle = \exp\{-j(j+1)\overline{\mathcal{D}}_z t\}, \quad (\text{A5})$$

where $\overline{\mathcal{D}}_z = (\mathcal{D}_x + \mathcal{D}_y)/2$. Eqs. (A1) and (A5) are identical for $j = 1$. For $j = 2$, numerics show that the approximate Eq. (A5) delivers OCFs which are virtually indistinguishable from their exact counterparts (A2).

OCFs $\langle P_j(\mathbf{u}_x(0)\mathbf{u}_x(t)) \rangle$ and $\langle P_j(\mathbf{u}_y(0)\mathbf{u}_y(t)) \rangle$ are obtainable from Eqs. (A1), (A2), and (A5) by the cyclic permutation of indexes x, y, z . Evidently, the generalized diffusion OCFs are also calculated via Eqs. (A1)-(A5), if we replace the diffusion coefficients \mathcal{D}_a by their rank-dependent counterparts \mathcal{D}_a^j (23).

The orientational relaxation times are defined as

$$\tau_a^j = \int_0^\infty dt \langle P_j(\mathbf{u}_a(0)\mathbf{u}_a(t)) \rangle. \quad (\text{A6})$$

According to Eq. (A5),

$$\tau_a^j = \{j(j+1)\overline{\mathcal{D}}_a^j\}^{-1}. \quad (\text{A7})$$

If all three $\tau_x^j, \tau_y^j, \tau_z^j$ are known, we can use Eq. (A7) to calculate the generalized diffusion coefficients through the formula

$$\mathcal{D}_x^j = \frac{1}{j(j+1)} \left\{ \frac{1}{\tau_y^j} + \frac{1}{\tau_z^j} - \frac{1}{\tau_x^j} \right\}. \quad (\text{A8})$$

\mathcal{D}_y^j and \mathcal{D}_z^j are obtained from Eq. (A8) by the cyclic permutation of x, y, z .

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TABLE I: Small-angle diffusion coefficients \mathcal{D}_a (in ps^{-1}) and integral orientational relaxation times $\tau_a^{(j)}$ (in ps) simulated in Ref.³⁸ for SPC/E water at a room temperature. The projections $a = x, y, z$ correspond to axis of the small, intermediate, and large moments of inertia of the water molecule.

| a | x | y | z |
|-----------------|------|------|------|
| \mathcal{D}_a | 0.46 | 0.45 | 0.22 |
| $\tau_a^{(1)}$ | 4.46 | 4.54 | 2.90 |
| $\tau_a^{(2)}$ | 2.00 | 1.57 | 1.17 |

TABLE II: The generalized diffusion model. Angular momentum relaxation times $\tau_{J,a}^{(0)}$ (in fs) and generalized angular momentum relaxation times $\tau_{J,a}^{(1)}, \tau_{J,a}^{(2)}$ (in fs) calculated from the data of Table I via Eqs. (25) and (A8).

| a | x | y | z |
|--------------------|------|------|------|
| $\tau_{J,a}^{(0)}$ | 1.13 | 2.07 | 1.55 |
| $\tau_{J,a}^{(1)}$ | 0.42 | 0.80 | 0.35 |
| $\tau_{J,a}^{(2)}$ | 0.40 | 0.55 | 0.33 |

TABLE III: The jump diffusion model. Jump times ν^{-1} (in ps) and jump angles g_a (in degrees) calculated from the data of Table I as is explained in the text.

| a | x | y | z |
|------------|------|------|------|
| ν^{-1} | 1.87 | 0.24 | 0.85 |
| g_a | 68 | 23 | 56 |